

CLAIMS:

1. A method for making a catalyst support with an enhanced hydrothermal stability comprising
 - a) forming a mixture comprising a boehmite material and a compound of at least one structural stabilizer;
 - b) drying the mixture to form a dried mixture, wherein the dried mixture comprises the boehmite material and the at least one structural stabilizer; and
 - c) calcining the dried mixture to form the stabilized support.
2. The method according to claim 1 wherein the mixture has a total mixture weight, and wherein the mixture has a solid content of from about 20% to about 60% by weight of the total mixture weight.
3. The method according to claim 1 wherein the mixture comprises water.
4. The method according to claim 3 wherein the mixture has a pH below about 7.
5. The method according to claim 4 wherein the mixture has a pH between about 3 and about 7.
6. The method according to claim 5 wherein the mixture has a pH between about 4 and about 6.

7. The method according to claim 3 further comprising adjusting the pH of the mixture to a pH value between about 4 and about 6 after forming the mixture.
8. The method according to claim 7 wherein the pH of the mixture is adjusted by adding acetic acid, nitric acid, formic acid, boric acid, or combinations thereof.
9. The method according to claim 1 wherein the mixture comprises an organic solvent.
10. The method according to claim 9 wherein the organic solvent comprises methanol, acetone, or ethanol.
11. The method according to claim 1 wherein drying is performed in a spray drier.
12. The method according to claim 1 wherein drying is performed in a conventional oven.
13. The method according to claim 12 wherein drying is performed at a temperature between about 75 °C and about 200 °C.
14. The method according to claim 1 wherein calcining is performed in an oxidizing atmosphere.
15. The method according to claim 1 wherein calcining is performed at a temperature between about 300 °C and about 900 °C.

16. The method according to claim 15 wherein calcining is performed at a temperature between about 500 °C and about 800 °C.
17. The method according to claim 1 further comprising d) applying an additional amount of a structural stabilizer to the stabilized support.
18. The method according to claim 17 wherein the structural stabilizer applied in step d) is the same as the at least one structural stabilizer used in step a).
19. The method according to claim 17 wherein the structural stabilizer applied in step d) is different than the at least one structural stabilizer used in step a).
20. The method according to claim 1 wherein the boehmite is derived as synthetic boehmite.
21. The method according to claim 1 wherein the boehmite is spray-dried boehmite or extruded boehmite.
22. The method according to claim 1 wherein the boehmite is dispersible.
23. The method according to claim 1 wherein the boehmite is non-dispersible.

24. The method according to claim 1 wherein the compound of the at least one structural stabilizer includes a salt of the at least one structural stabilizer, an acid of the at least one structural stabilizer, an oxide of the at least one structural stabilizer, or combinations thereof.

25. The method according to claim 1 wherein the structural stabilizer comprises at least one element selected from the group consisting of tungsten (W), tantalum (Ta), niobium (Nb), thorium (Th), germanium (Ge), uranium (U), tin (Sn), antimony (Sb), vanadium (V), hafnium (Hf), sodium (Na), potassium (K), boron (B), magnesium (Mg), aluminum (Al), silicon (Si), calcium (Ca), titanium (Ti), chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn), gallium (Ga), strontium (Sr), zirconium (Zr), barium (Ba), thorium (Th), lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), lutetium (Lu), oxides thereof, and combinations thereof.

26. The method according to claim 1 wherein the structural stabilizer comprises at least one element selected from the group consisting of cobalt, magnesium, zirconium, boron, aluminum, barium, silicon, lanthanum, oxides thereof, and any combination thereof.

27. The method according to claim 1 wherein the structural stabilizer comprises at least one element selected from the group consisting of cobalt, magnesium, zirconium, boron, barium, silicon, lanthanum, oxides thereof, and any combination thereof.

28. The method according to claim 1 wherein the structural stabilizer includes a co-precipitated silica-alumina.
29. The method according to claim 28 wherein the co-precipitated silica-alumina has a molar ratio of silica to alumina between about 1:1 and about 500:1.
30. The method according to claim 1 wherein the stabilized support has an average pore size larger than about 4 nm.
31. The method according to claim 1 wherein the stabilized support has an average pore size between about 4 nm and about 20 nm.
32. The method according to claim 1 wherein the stabilized support has a surface area larger than 30 m² per gram of support.
33. The method according to claim 1 wherein the stabilized support has a surface area between about 50 m² per gram of support and about 250 m² per gram of support.
34. The method according to claim 1 wherein the stabilized support is in the form of particles.
35. The method according to claim 34 wherein the particles have a range of sizes between about 10 microns and about 200 microns.

36. The method according to claim 34 wherein the stabilized support has an average size of the particles between about 50 microns and about 90 microns.

37. The method according to claim 34 wherein the particles include a plurality of crystallites with an average size between about 10 and about 40 nm.

38. The method according to claim 34 wherein the particles have sizes greater than 0.5 millimeter.

39. The method according to claim 1 wherein forming the mixture of step a) further comprises dispersing the boehmite material in a solvent to form a sol and adding the compound of the at least one structural stabilizer to the sol.

40. The method according to claim 1 wherein forming the mixture of step a) further comprises dispersing the compound of the at least one structural stabilizer in a solvent to form a sol and adding the boehmite material to the sol.

41. The method according to claim 1 wherein forming the mixture of step a) further comprises dispersing the boehmite material in a first solvent to form a first sol, dispersing the compound of the at least one structural stabilizer in a second solvent to form a second sol or a solution, and combining the first sol with the second sol or the solution.

42. The method according to claim 1 wherein step b) further comprises:

(1) treating the dried mixture to form a dried mixture comprising a partially-stabilized support; and

(2) applying a portion of the at least one structural stabilizer to the dried mixture comprising the partially-stabilized support to form a dried mixture comprising a support precursor,

and wherein the dried mixture of step c) comprises the dried mixture comprising the support precursor.

43. A method for making a catalyst support with an enhanced hydrothermal stability comprising

a) dispersing the boehmite in a solvent to form a sol;

b) drying the sol to form a dried boehmite;

c) depositing a compound of a structural stabilizer to the dried boehmite to form a support precursor, wherein the support precursor comprises boehmite and the structured stabilizer; and

d) treating the support precursor to form a stabilized support.

44. The method according to claim 43 wherein the sol has a total sol weight, and wherein the sol has a solid content of from about 20% to about 40% by weight of the total sol weight.

45. The method according to claim 43 wherein the solvent comprises water.

46. The method according to claim 43 wherein the solvent comprises methanol, acetone, or ethanol.

47. The method according to claim 43 wherein drying is performed in a spray drier or in a conventional oven.
48. The method according to claim 43 wherein drying is performed at a temperature between about 75 °C and about 200 °C.
49. The method according to claim 43 wherein depositing is accomplished by impregnation, precipitation, or chemical vapor deposition.
50. The method according to claim 43 wherein treating includes calcining the support precursor in an oxidizing atmosphere at a temperature between about 300 °C and about 900 °C.
51. The method according to claim 43 wherein the boehmite is synthetic boehmite.
52. The method according to claim 43 wherein the boehmite is calcined at a temperature between about 250 °C to about 350 °C before depositing the compound of the structural stabilizer of step c).
53. The method according to claim 43 wherein the structural stabilizer comprises at least one element selected from the group consisting of tungsten (W), tantalum (Ta), niobium (Nb), thorium (Th), germanium (Ge), uranium (U), tin (Sn), antimony (Sb), vanadium (V), hafnium (Hf), sodium (Na), potassium (K), boron (B), magnesium (Mg), aluminum (Al), silicon (Si), calcium (Ca), titanium (Ti), chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu),

zinc (Zn), gallium (Ga), strontium (Sr), zirconium (Zr), barium (Ba), thorium (Th), lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), lutetium (Lu), oxides thereof, and combinations thereof.

54. The method according to claim 43 wherein the structural stabilizer is selected from the group consisting of cobalt, magnesium, zirconium, boron, barium, silicon, lanthanum, oxides thereof, and combinations thereof.

55. A catalyst for the production of hydrocarbons from synthesis gas comprising
a catalytically active metal selected from the group consisting of cobalt, ruthenium, iron, nickel, and combinations thereof;
optionally, a promoter; and
a stabilized support prepared by a method comprising forming a mixture comprising a boehmite material and at least one structural stabilizer compound, drying the mixture, and calcining the dried mixture,
wherein the stabilized support has an average pore size larger than 4 nm and a surface area larger than 30 m² per gram of support.

56. The catalyst according to claim 55 wherein the stabilized support is in the form of particles.

57. The catalyst according to claim 56 wherein the particles have sizes between about 10 microns and about 200 microns.

58. The catalyst according to claim 56 wherein the stabilized support has an average size of the particles between about 50 microns and about 90 microns.

59. The catalyst according to claim 56 wherein the particles include a plurality of crystallites with an average size between about 10 nm and about 40 nm.

60. The catalyst according to claim 55 wherein the catalytically active metal is cobalt.

61. The catalyst according to claim 60 wherein the promoter comprises rhenium, ruthenium, platinum, palladium, boron, silver, or combinations thereof.

62. The catalyst according to claim 55 wherein the structural stabilizer comprises at least one element selected from the group consisting of tungsten (W), tantalum (Ta), niobium (Nb), thorium (Th), germanium (Ge), uranium (U), tin (Sn), antimony (Sb), vanadium (V), hafnium (Hf), sodium (Na), potassium (K), boron (B), magnesium (Mg), aluminum (Al), silicon (Si), calcium (Ca), titanium (Ti), chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn), gallium (Ga), strontium (Sr), zirconium (Zr), barium (Ba), thorium (Th), lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), lutetium (Lu), oxides thereof, and combinations thereof.

63. The catalyst according to claim 55 wherein the structural stabilizer comprises at least one element selected from the group consisting of cobalt, magnesium, zirconium, boron, aluminum, barium, silicon, lanthanum, oxides thereof, and any combination thereof.
64. The catalyst of claim 55, wherein the structural stabilizer includes a co-precipitated silica-alumina.
65. The catalyst according to claim 64 wherein the co-precipitated silica-alumina has a molar ratio of silica to alumina between about 1:1 and about 500:1.
66. A process for the production of hydrocarbons from synthesis gas comprising
converting a mixture of hydrogen and carbon monoxide to a product stream comprising hydrocarbons in a reactor comprising a hydrocarbon synthesis catalyst,
wherein the hydrocarbon synthesis catalyst comprises
a catalytically active metal selected from the group consisting of cobalt, ruthenium, iron, nickel, and combinations thereof;
optionally, a promoter; and
a stabilized support prepared by a method comprising drying and calcining a mixture containing a boehmite material and a structural stabilizer.
67. The process according to claim 66 wherein the structural stabilizer comprises at least one element selected from the group consisting of tungsten (W), tantalum (Ta), niobium (Nb), thorium (Th), germanium (Ge), uranium (U), tin (Sn), antimony (Sb), vanadium (V), hafnium (Hf), sodium

(Na), potassium (K), boron (B), magnesium (Mg), aluminum (Al), silicon (Si), calcium (Ca), titanium (Ti), chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn), gallium (Ga), strontium (Sr), zirconium (Zr), barium (Ba), thorium (Th), lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), lutetium (Lu), oxides thereof, and combinations thereof.

68. The process according to claim 66 wherein the structural stabilizer is selected from the group consisting of cobalt, magnesium, zirconium, boron, barium, silicon, lanthanum, oxides thereof, and any combination thereof.

69. The process according to claim 66 wherein the structural stabilizer includes a co-precipitated silica-alumina.

70. The process according to claim 69 wherein the co-precipitated silica-alumina has a molar ratio of silica to alumina between about 1:1 and about 500:1.

71. The process according to claim 66 wherein the stabilized support is in the form of particles.

72. The process according to claim 71 wherein the reactor is a slurry bed reactor or fluidized bed reactor, and the stabilized support has a range of particles sizes between about 10 microns and about 200 microns.

73. The process according to claim 71 wherein the reactor is a fixed bed reactor, and the stabilized support has a range of particles sizes greater than 0.5 mm.
74. The process according to claim 71 wherein the stabilized support has an average size of the particles between about 50 microns and about 90 microns.
75. The process according to claim 71 wherein the particles include a plurality of crystallites with an average size between about 10 nm and about 40 nm.
76. The process according to claim 66 wherein the catalytically active metal is cobalt.
77. The process according to claim 76 wherein the promoter comprises rhenium, ruthenium, platinum, palladium, boron, silver, or combinations thereof.
78. The process according to claim 66 wherein the mixture has a pH between about 4 and about 6.
79. The process according to claim 66 wherein drying is performed in a spray drier or in a conventional oven.
80. The process according to claim 66 wherein drying is performed at a temperature between about 75 °C and about 200 °C.

81. The process according to claim 66 wherein calcining the mixture of boehmite material and the structural stabilizer is performed in an oxidizing atmosphere at a temperature between about 300 °C and about 900 °C.

82. The process according to claim 66 wherein calcining is accomplished at a temperature between about 500 °C and about 800 °C.

83. The process according to claim 66 wherein the reactor is a Fischer-Tropsch reactor operated at a temperature from about 190°C to about 260°C, and a pressure between about 552 kPa and about 6,895 kPa.

84. The process according to claim 66 wherein the product stream comprises hydrocarbons having 5 or more carbon atoms.